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(21) International Application Number: PCT/SE94/00807 (22) International Filing Date: 2 September 1994 (02.09.94) (30) Priority Data: 9302912-2 9 September 1993 (09.09.93) SE (71) Applicant (for all designated States except US): PERSTORP AB [SE/SE]; S-284 80 Perstorp (SE). (72) Inventor; and (75) Inventor/Applicant (for US only): OLSSON, Per [SE/SE]; Arvid Lindmansgatan 2 A, S-417 26 Göteborg (SE). (74) Agent: STENBERG, Yngve; Perstorp AB, S-284 80 Perstorp (SE).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: A CATALYST MATERIAL FOR PURIFICATION OF GASES AND LIQUIDS AND A PROCESS FOR PREPARING IT		
(57) Abstract <p>A catalyst material for purification of gases and liquids and a process for preparing it. The catalyst material includes a catalytically inert support body with at least one metal oxide coating deposited on the support body. The support body consists of a ceramic material with a macropore system as well as a micro- and/or a mesopore system. The ceramic material is produced by mixing clay, preferably kaolin, with at least one combustible material, which mixture by means of pelletizing, extruding or the like is formed to bodies, which are burnt at a temperature preferably within the range of 1000-1200 °C. One or more metal oxides are deposited on the support bodies by impregnating them with an aqueous solution of at least one metal salt, whereupon the metal salt by contact with one or more alkaline substances is precipitated as a metal hydroxide. The support bodies are subsequently dried and heated to a temperature of 200-900 °C, whereby the precipitated metal hydroxyde is calcined to the corresponding oxide.</p>		

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A catalyst material for purification of gases and liquids and a process for preparing it.

This invention relates to a catalyst material, a process for preparing it and a use thereof. The catalyst material comprises a catalytically inert support body and at least one on the support body deposited metal oxide coating.

From the U.K. patent No. 1 430 952 it is known to impregnate a support body with an aqueous solution of a metal salt, and then by means of one or more alkaline substances precipitate a metal hydroxide from the metal salt, and subsequently calcine the support body whereby the precipitated metal hydroxide is calcined to the corresponding oxide. The principal advantage of the method according to the U.K. patent is that a tightly-adhering metal oxide coating is obtained on the support without the need for binders. The support bodies which are principally referred to in this patent are of the honeycomb type with thin channels.

For a long time catalysts have been described in the literature. In these catalysts the active compound often consists of at least one metal and/or metal oxide. Various structures and functions are known. Important factors for such a catalyst is of the pore size distribution and the size of the surface area, which both affect the efficiency and the activity of the catalyst. Coarse pores and the highest possible specific surface area are desired. Coarse pores result in a highly efficient diffusibility which makes the catalyst more efficient since transport limitations are reduced. Further a high surface area results in a higher catalytic activity as the area of contact between the catalytically active phase and for instance a gas

increases. To obtain a high efficiency and a high activity at the same time the catalyst should consequently be characterised in macropores combined with a high surface area.

At the production of catalysts one usually starts from an inert support body, often a ceramic material. The support body is coated with at least one metal oxide and/or metal.

At present there are problems at the production of catalysts with ceramic support bodies, principally in the form of pellets, which both have a high surface area and a highly efficient diffusibility. The problem is that in order to obtain a high surface area, and thereby a high activity, the pellets have been provided with a higher amount of pores and the pores have been made smaller. This in its turn has implied that, because of mass transport limitations, the effective diffusion has decreased and the transformation degree of the catalyst has then become unchanged or decreased instead of increased. Pellet catalyst with a high surface area and a highly efficient diffusibility are especially suitable in applications where a high internal mass transport is of great importance as for instance at total oxidation of hydrocarbons comprised in for instance stackgases and at desulphurisation of petroleum fractions such as combustible oils, naphta and the like.

At the traditional process for the production of pellet catalysts the support bodies are impregnated with a metal salt, dried and burned, whereby the metal salt is calcined to the corresponding oxide. Then the surface area of the support body, irrespective of the magnitude of the pores,

does not get much larger than the total surface area of the pores. When the poresystem of the support body is a micro- or a mesoporesystem, the pores become very narrow with a resulting low diffusibility.

The coating with an active phase of a metal is usually obtained by immersing the support body into a solution of a metal salt, which is subsequently reduced under heating in an atmosphere containing hydrogen for instance. Before the deposition of the active phase the support body is often coated with a catalytically inactive phase, for instance a catalytically inactive metal oxide, which constitutes an underlayer for the active phase.

According to the present invention it has surprisingly become possible to solve the above problem with pellet catalysts and a process for preparing a catalyst material including a catalytically inert support body, with at least one on the support body deposited metal oxide coating has been brought about. The catalyst is characterised in that the support body consists of a ceramic material which is produced by mixing clay, preferably kaolin, with at least one combustible material. The mixture is formed by means of pelletizing, extrusion or the like to bodies such as pellets, granules or tablets, preferably pellets, which are burnt at a temperature exceeding the biscuit firing temperature but below the incrustation heat of the clay, preferably within the range of 1000-1200°C. When the bodies are burnt the combustible material is released and ceramic support bodies with a macroporesystem is obtained. One or more metal oxides are then deposited on the support bodies by impregnating them with an aqueous solution of at least one metal salt, preferably a chloride

or nitrate salt, whereupon the metal salt by contact with one or more alkaline substances, preferably an aqueous solution of sodium hydroxide, potassium hydroxide, calcium hydroxide or ammonia is precipitated as the corresponding metal hydroxide. After the precipitation the support bodies are dried and heated to a temperature of 200-900°C, preferably 500-700°C, whereby the precipitated metal hydroxide is principally calcined to the corresponding oxide, resulting in support bodies with a micro- and/or mesoporesystem in the macroporesystem.

A liquid, preferably water may be added to the clay and the combustible material to obtain a mouldable paste.

The bodies formed are often dried before the burning step.

The support bodies can for instance be produced by means of a tablet machine, a disc palletizer or two rollers.

The macroporesystem formed in the support bodies, preferably pellets in combination with the pronounced increase of the catalytically active surface area which is considerably higher than the original surface area results in a highly efficient diffusibility and a high overall activity at the same time.

According to the invention it has been possible to combine coarse pores with high efficient diffusibility with a high surface area and thereby a high activity.

By an alkaline precipitation of the metal salt as a hydroxide before the calcination a voluminous precipitate

is obtained on the support bodies and in their poresystem. The swelling of the hydroxide precipitate that occurs as a result of the chemical reactions makes the surface of the metal oxide coating increase considerably after the calcination. Thus, the surface area has increased considerably to very strongly in relation to the deposited amount of oxide and to the surface structure of the pores. The degree of the swelling is dependent upon the choice of metal salt, i.e. which positive respectively negative ion the metal salt contains, and the choice of the base for the precipitation.

The metal salts are present as aqueous solutions. Therefore, also the precipitation agents, the alkaline substances are preferably used as aqueous solutions. Normally the whole support bodies are immersed into respectively solution.

As mentioned above ammonia solution and/or alkali metal hydroxides are adequate precipitating agents. Ammonia is preferred, unless the metal salt is soluble or partly soluble therein, forms complex compounds with ammonia or ammonia in another way causes problems. If ammonia solution is used for the precipitation of a metal chloride for instance a precipitate of ammonium chloride is obtained on the support bodies in addition to the metal hydroxide. The precipitated ammonium chloride is released from the support bodies at the calcination. If a hydroxide is used, for instance sodium hydroxide, sodium chloride is obtained which must be washed away before the calcination of the metal hydroxide, i.e. an extra production step is needed.

Advantageously the combustible material consists of graphite and/or cellulose in a weight ratio of 60:40-40:60 in relation to the clay. The combustible material has suitably an average particle size of 1-100 μ m, preferably 30-70 μ m.

In one embodiment of the invention the metal oxide coating consists of one or more catalytically active oxides of metals such as nickel, cobalt, manganese, iron, copper, chromium and/or molybdenum. In that case the catalyst, consisting of a micro- and/or mesoporesystem and a macroporesystem, is activated and ready to be used directly after the calcination.

In one alternative embodiment of the invention the metal oxide coating consists of one or more catalytically inactive metal oxides, preferably oxides of aluminium and/or titanium. In this case a semi-finished catalyst material is obtained consisting of a bimodally poresystem, i.e. a micro- or mesoporesystem and a macroporesystem. The support bodies are then catalytically activated by depositing a least one catalytically active phase in the form of a metal oxide, a metal sulphide or a metal from at least one of the groups

- (i) nickel, cobalt, manganese, iron, copper, chromium and/or molybdenum;
- (ii) platina, palladium and/or rhodium;

on the support bodies and in the poresystem thereof. The inactive metal oxide coating functions as a subcoating and causes the desired enlargement of the active surface area.

It is possible according to the invention to deposit two or more metal oxide coatings with or without calcination in between.

According to another embodiment of the invention the catalytically active oxide can be converted to sulphide. The oxide can consist of molybdenum oxide, combined with nickel oxide and/or cobalt oxide.

At the activation step metal oxides and metals can be deposited by most of the methods known in the art.

The active phase of the catalysts can be achieved with a catalytically active metal oxide, mixtures of different active oxides of the same metal and/or different metals. Combinations of different oxides are obtained by the use of mixtures of metal salts or by the deposition of several layers with or without calcination in between. Furthermore, different combinations of catalytically inactive metal oxides and catalytically active metal oxides or metals can be used. Such combinations are deposited in different layers, preferably with a calcination in between. By the use of different metal oxides, different combinations of metal oxides or different combinations of metal oxides and metals, for instance the efficiency, the activity and the working life of the catalyst can be adapted to various needs. CO_3O_4 deposited according to the invention results in a very efficient catalyst with a comparatively short working life, while the combination of underlaying TiO_2 deposited according to the invention and metallic copper deposited according to a known method results in a somewhat lower efficiency but a considerably longer working life.

The catalyst material according to the invention can be used for purification of gases and liquids, such as at total oxidation of hydrocarbons comprised in for instance stack-gases and at desulphurisation of petroleum fractions such as combustible oils, naphta and the like.

The invention is further explained by the following examples and the enclosed Figures 1 and 2, where Example 1 shows the production of a ceramic support body in the form of pellets with a macroporesystem.

Example 2 shows a deposition according to the present invention of a catalytically active metal oxide (CO_3O_4) on the support body obtained according to Example 1.

Example 3 shows the production of a catalytically inactive support body by deposition according to the present invention of a catalytically inactive metal oxide (Al_2O_3) on the pellets obtained according to Example 1.

Example 4 shows the activation of the pellets produced according to Example 3 by deposition of a catalytically active metal oxide (CuO).

Example 5 shows the activation of the pellets produced according to Example 3 by deposition of metallic palladium.

Example 6 shows the catalytic activity of a Pd catalyst according to Example 5 in comparison with the catalytic activity of a traditional Pd catalyst consisting of pellets of Al_2O_3 with a microporesystem coated with metallic palladium.

Example 7 shows the catalytic activity of a Co_3O_4 catalyst according to Example 2 in comparison with the catalytic activity of a Co_3O_4 catalyst consisting of pellets of Co_3O_4 having a microporesystem.

Figures 1 and 2 illustrate the result obtained according to Examples 6 and 7.

Example 1

A ceramic support body was produced by mixing dry kaolin with graphite having an average particle size of 50 μm , in a weight ratio of 1:1. The obtained powder was mixed with water to a mouldable paste which by means of extrusion was shaped to small bodies in the form of cylinders, so called pellets. The bodies were dried and burnt at a temperature of 1100°C (the biscuit firing temperature was about 800°C and the incrustation heat of the clay was 1150-1350°C).

At the burning the combustible graphite was released and a coarse-porous (macropore-) system was formed in the resulting ceramic material.

The obtained ceramic pellets had an average diameter of 2 mm, a length of 4-10 mm and a surface area of approximately 2 m^2/g .

Example 2

The ceramic pellets obtained according to Example 1 were immersed for 1 hour in a 15 % aqueous solution of CoCl_3 . The pellets were picked up and afterwards immersed for 1

hour in a 5 M aqueous solution of NaOH whereby $\text{Co}(\text{OH})_3$ and NaCl were precipitated on the pellets and in the pore system of the pellets. The pellets were picked up and the NaCl formed was washed away with water. After the washing the pellets were dried and burnt at a temperature of 500°C , whereby $\text{Co}(\text{OH})_3$ was calcined to Co_3O_4 . In this way an activated catalyst was obtained.

Example 3

Ceramic pellets obtained according to Example 1 were immersed for 1 hour in a 10 % aqueous solution of AlCl_3 . The pellets were picked up and then immersed for 1 hour in a 10 % aqueous solution of ammonia whereby $\text{Al}(\text{OH})_3$ and NH_4Cl were precipitated on the pellets and in the pore-system of the pellets. The pellets were picked up, dried and burnt at a temperature of 500°C , whereby $\text{Al}(\text{OH})_3$ was calcined to Al_2O_3 and the NH_4Cl was released. A catalytically inactive carrier with a macroporesystem and a micro/mesoporesystem was obtained. The surface area of the pellets increased from approximately $2 \text{ m}^2/\text{g}$ before the application of Al_2O_3 to approximately $50 \text{ m}^2/\text{g}$ afterwards.

Example 4

The pellets obtained according to Example 3 were activated by immersing them for 1 hour in a 10 % aqueous solution of $\text{Cu}(\text{NO}_3)_2$. The pellets were picked up, dried and burnt at a temperature of 500°C , whereby the $\text{Cu}(\text{NO}_3)_2$ absorbed on the pellets and in the poresystem of the pellets was calcined to CuO. In this way an activated catalyst was obtained.

Example 5

The pellets obtained according to Example 3 were activated with a coating of metallic palladium, which was deposited by immersing the pellets for 2 minutes in an aqueous solution of PdCl_2 (20 $\mu\text{mol/l}$) and afterwards reducing PdCl_2 to metallic palladium at 400°C in an atmosphere containing 1 % propane.

Example 6

A conventional Pd catalyst was produced by coating a conventional Al_2O_3 pellet shaped carrier with a surface area of 200 m^2/g with metallic palladium. The catalyst was charged into a reactor for measuring the conversion of CO-gas into CO_2 -gas when the CO gas passed the reactor. The conversion of CO was measured in percentage as a function of the inlet temperature of the CO-gas into the reactor.

The process was repeated with the Pd catalyst produced according to Example 5.

The results obtained with the above two catalysts are shown on the enclosed Figure 1 as two curves. From a comparison of the two curves it is evident that the catalytic activity of the Pd catalyst according to the invention exceeds the catalytic activity of the conventional Pd catalyst at all temperatures in the test.

The catalyst according to the invention has the advantages as compared to a conventional catalyst that the degree of conversion of CO into CO_2 is higher and that the catalyst can work at a lower temperature.

Example 7

The test disclosed in Example 6 was repeated but other catalysts were compared. Thus in this case the catalytic activity of a CO_3O_4 catalyst produced according to Example 2 was compared with a conventional CO_3O_4 catalyst consisting of pellets of CO_3O_4 with a microporesystem and a surface area of about $150 \text{ m}^2/\text{g}$.

The results obtained are illustrated by the curves on the enclosed Figure 2. As shown the catalytic activity of the CO_3O_4 catalyst of the invention exceeds the catalytic activity of the conventional CO_3O_4 catalyst at all temperatures in the test.

Also this experiment shows that the catalyst according to the invention has the advantages as compared to the conventional catalyst that the degree of conversion of CO into CO_2 is higher and that the catalyst can work at a lower temperature.

The present invention is not limited to the embodiments shown, since these can be modified in different ways within the scope of the invention.

CLAIMS

1. A process for preparing a catalyst material including a catalytically inert support body, with at least one on the support body deposited metal oxide coating, characterised in, that the support body consists of a ceramic material, which material is produced by mixing clay, preferably kaolin, with at least one combustible material, which mixture by means of pelletizing, extruding or the like is formed to bodies such as pellets, granules or tablets, preferably pellets, which bodies are burnt at a temperature exceeding the biscuit firing temperature but below the incrustation heat of the clay, preferably within the range of 1000-1200°C, at which heating the combustible material is released and ceramic support bodies with a macroporesystem is obtained, that one or more metal oxides are deposited on the support bodies by impregnating them with an aqueous solution of at least one metal salt, preferably a chloride or nitrate salt, whereupon the metal salt by contact with one or more alkaline substances, preferably an alkalimetal hydroxide solution or an ammonia solution is precipitated as a metal hydroxide, and that the support bodies are subsequently dried and heated to a temperature of 200-900°C, preferably 500-700°C, whereby the precipitated metal hydroxide is principally calcined to the corresponding oxide and support bodies with a micro- and/or a mesoporesystem in the macroporesystem are obtained.
2. A process according to claim 1 characterised in, that a liquid, preferably water is mixed with the clay and the combustible material.

3. A process according to claim 1 or 2 c h a r a c t e r i s e d i n, that the bodies formed are dried before the burning step.
4. A process according to anyone of claims 1-3 c h a r a c t e r i s e d i n, that the combustible material consists of graphite and/or cellulose in a weight ratio of 60:40-40:60 in relation to the clay.
5. A process according to anyone of claims 1-4 c h a r a c t e r i s e d i n, that the average particle size of the combustible material is 1-100 μm , preferably 30-70 μm .
6. A process according to anyone of claims 1-5 c h a r a c t e r i s e d i n, that the metal oxide coating consists of one or more catalytically active oxides of metals such as nickel, cobalt, manganese, iron, copper, chromium and/or molybdenum, whereby a catalyst with a micro- and/or mesoporesystem is obtained.
7. A process according to anyone of claims 1-5 c h a r a c t e r i s e d i n, that the metal oxide coating consists of one or more catalytically inactive metal oxides, preferably oxides of aluminium and/or titanium, whereby a catalytically inactive support body with a micro- and/or mesoporesystem and a macroporesystem is obtained.
8. A process according to anyone of claims 1-7 c h a r a c t e r i s e d i n, that two or more metal oxide coatings are deposited with or without calcination in between.

9. A process according to anyone of claims 7 or 8 characterised in, that the support body is catalytically activated by depositing at least one catalytically active phase of a metal such as an oxide or a sulphide from at least one of the groups

(i) nickel, cobalt, manganese, iron, copper, chromium and/or molybdenum;

(ii) platina, palladium and/or rhodium;

on the support body and in the poresystem thereof, whereby the previously deposited catalytically inactive metal oxide coating functions as a subcoating.

10. A process according to anyone of claims 6 or 9 characterised in, that the catalytically active oxide is converted into a sulphide.

11. A process according to claim 10 characterised in, that the catalytically active oxide is molybdenum oxide, combined with nickel oxide and/or cobalt oxide.

12. A process according to claim 7 or 8 characterised in, that the support body is activated catalytically by depositing at least one catalytically active metal from at least one of the groups

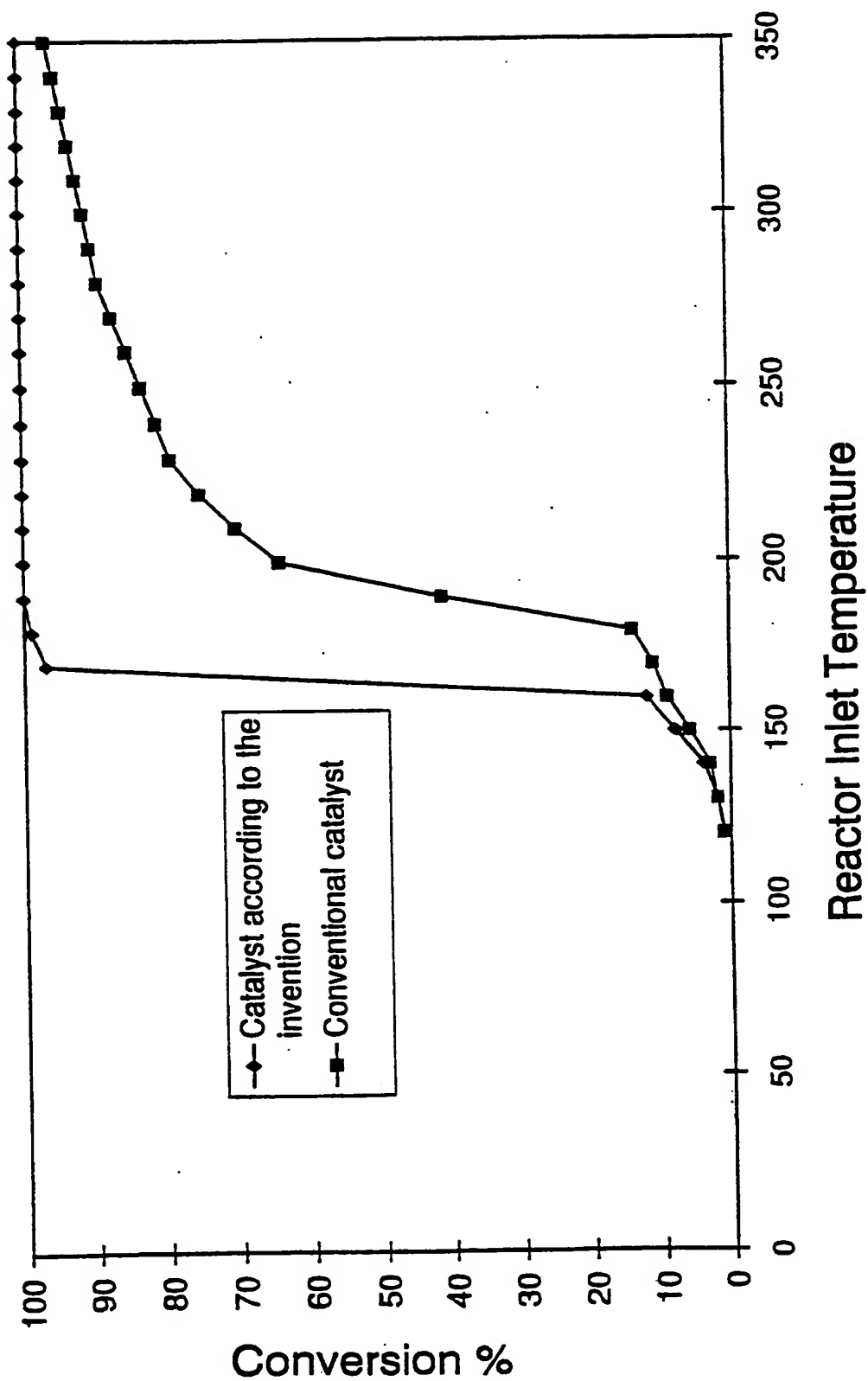
(i) nickel, cobalt, manganese, iron, copper, chromium and/or molybdenum;

(ii) platina, palladium and/or rhodium;

on the support body and in the poresystem thereof, whereby the previously deposited catalytically inactive metal oxide coating functions as a subcoating.

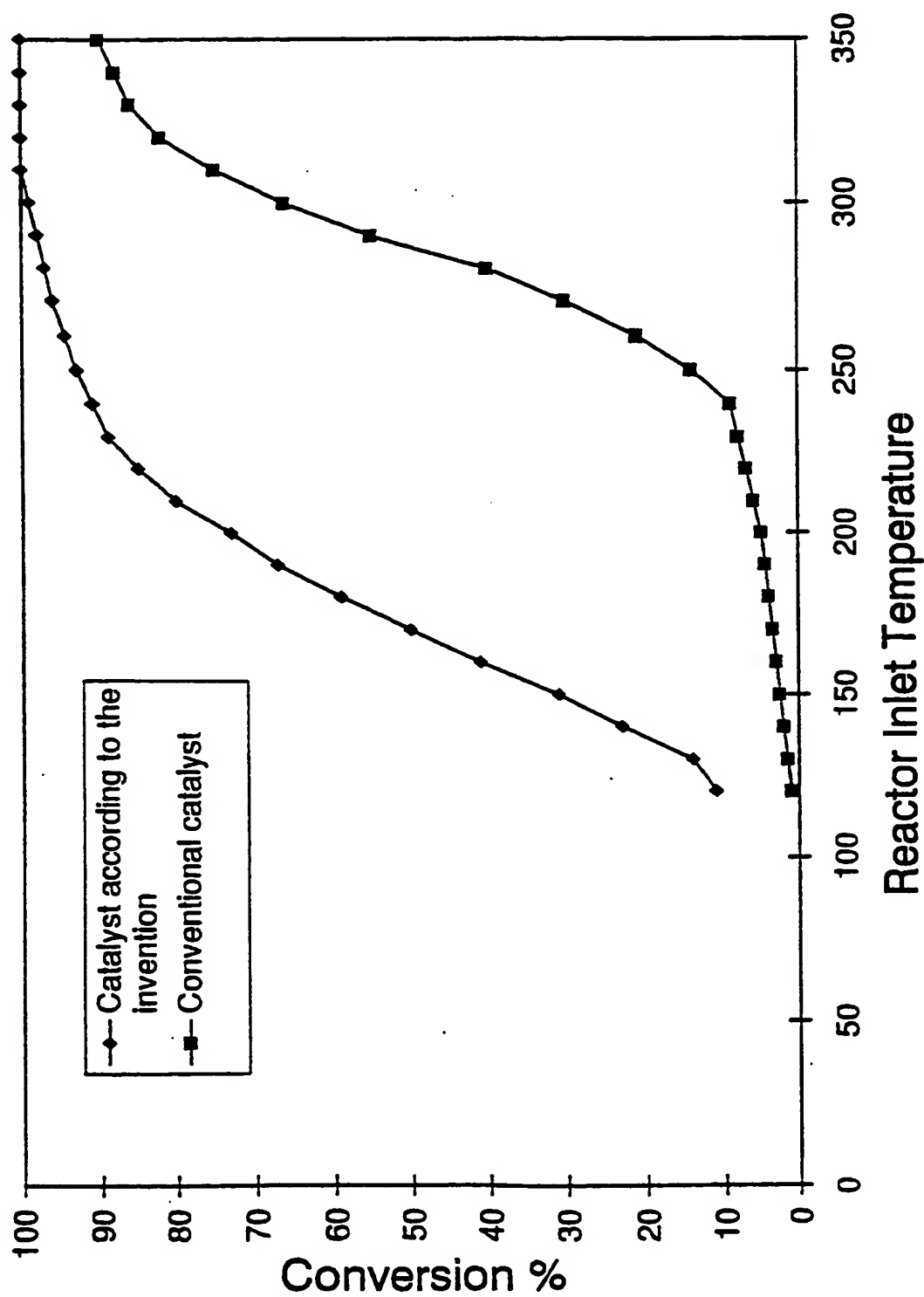
13. A catalyst material produced according to anyone of claims 1-12.
14. The use of a catalyst material according to claim 13 for purification of gases and liquids.

Fig. 1
CO Conversion for Pd Catalysts



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Fig. 2 **CO Conversion for Cobalt Catalysts**



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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 94/00807

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01J 37/03, B01J 35/10, B01J 21/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB, A, 1430952 (CORNING GLASS WORKS), 7 April 1976 (07.04.76), page 1, line 10 - line 22; page 1, line 77 - line 85; page 2, line 13 - line 37, page 2, line 59 - page 3, line 17, page 4, line 17 - line 18, page 4, line 72, claims 1,2,6 --	1-14
A	US, A, 4001143 (ELREY L. MCCANN, III), 4 January 1977 (04.01.77), column 1, line 6 - line 12; column 3, line 66 - column 6, line 12, claim 4 -- -----	1-14

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

29/10/94

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US-A- 4001143	04/01/77	CA-A- 1068250 JP-A- 51123795	18/12/79 28/10/76